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REVIEW PAPER

Ferrocenyl-terminated Dendrimers: Design for Applications in Molecular Electronics, Molecular Recognition and Catalysis

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Abstract This micro-review shows how a simple but powerful organometallic C–H activation could be made very useful for the construction of a large variety of stars, dendritic cores, dendrons and dendrimers of variable sizes including giant dendrimers and gold-nanoparticle-cored dendrimers. The synthesis of ferrocenyl-terminated dendrimers was then achieved by reactions of chlorocarbonylferrocene with polyamino dendrimers, ferrocenylsilylation of polyolefin dendrons and dendrimers and "click" reactions of ferrocenyl acetylene with azido-terminated dendrimers. The functions of these metallo-dendrimers include molecular electronics (molecular batteries), molecular redox recognition and sensing and catalysis using dendritic stabilization of nanoparticle catalysts.

Keywords Dendrimer · "Click" reaction · Ferrocene · Sensor · Catalysis · Nanoparticle

1 Introduction

Macromolecules bearing stable redox systems have potential for applications involving molecular electronics, sensors and catalysis [1]. What are the advantages of dendrimers [2] over polymers? They are perfectly defined macromolecules, i.e. their polydispersity is 1.00, a number of dendritic generations can be constructed for a given series [2], and they have a globular shape resulting in formidable encapsulation properties [3]. In a word, their supramolecular properties [4] are specific and well defined due to flexible design, and they allows them to achieve precise functions that are not accessible with polymers. This short review will illustrate these points and show how dendrimer design can lead to functions such as molecular recognition, catalysis and molecular electronics. Being originally hard-core organometallic chemists, our entry into the dendrimer field was serendipitous before the nanoscience fashion, and due to the discovery of a simple C–H activation system.

2 The Serendipitous Discovery of an Extremely Easy and Useful C–H Activation System

In 1979, we disclosed a family of stable 19-electron sandwich complexes [$Fe^ICp(\eta^6$-arene)], Cp = η^5-C_5H_5 that we called "Electron-reservoir" systems [5] because they are the most electron-rich neutral molecules (lowest known ionization potential values) [6] and both the Fe^I and Fe^{II} forms are stable. The C–H activation at a benzylic arene position results from contact with air within seconds at a temperature as low as −78 °C, producing the 18-electron Fe^{II} cyclohexadienyl complex bearing an exocyclic doubly bonded CH_2 group. If the reaction is carried out in an EPR tube, the intermediacy of superoxyde anion, $O_2^{\cdot-}$ is observed, which indicates that Fe^I has transferred an electron to O_2, leaving the 18-electron intermediate cation [$Fe^{II}Cp(\eta^6$-arene)]$^+$, with $O_2^{\cdot-}$ as the counter anion. This mechanism is confirmed by the use of KO_2 in the presence

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of 18-crown-6 ether to deprotonate the PF_6^- salt of this cation; and many standard bases such as *t*-BuOK and KOH do the same. The CH_2 group of the C–H activated product rapidly reacts as a mild nucleophile with a wide range of electrophiles under ambient conditions (Scheme 1) [7].

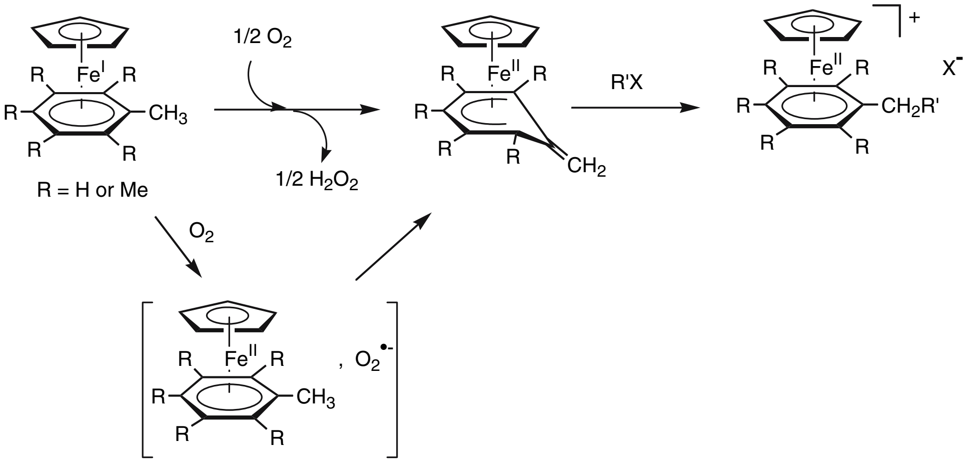
Moreover, we immediately found that when excess of *t*-BuOK and CH_3I were added to $[Fe^{II}Cp(\eta^6\text{-}C_6Me_6)]^+[PF_6]^-$ in THF at room temperature, the deprotonation–alkylation sequence was iterated six times in situ within a minute to quantitatively yield the complex in which all the six groups had undergone the deprotonation–methylation sequence to $[Fe^{II}Cp(\eta^6\text{-}C_6Et_6)]^+[PF_6]^-$ (Scheme 2) [5, 8].

It was exactly at the same time that Fritz Vögtle in Bonn reported the first dendritic iteration from a diamine to an octa-amine using the Michaël addition-hydride reduction sequence [9]. Upon similar allylation or benzylation the hexamethylbenzene complex $[Fe^{II}Cp(\eta^6\text{-}C_6Me_6)]^+[PF_6]^-$ directly leads to a large family of star-shaped molecules that can provide useful, recyclable star-shaped hexa-ligands and their catalytically extremely efficient palladium complexes (Scheme 3).

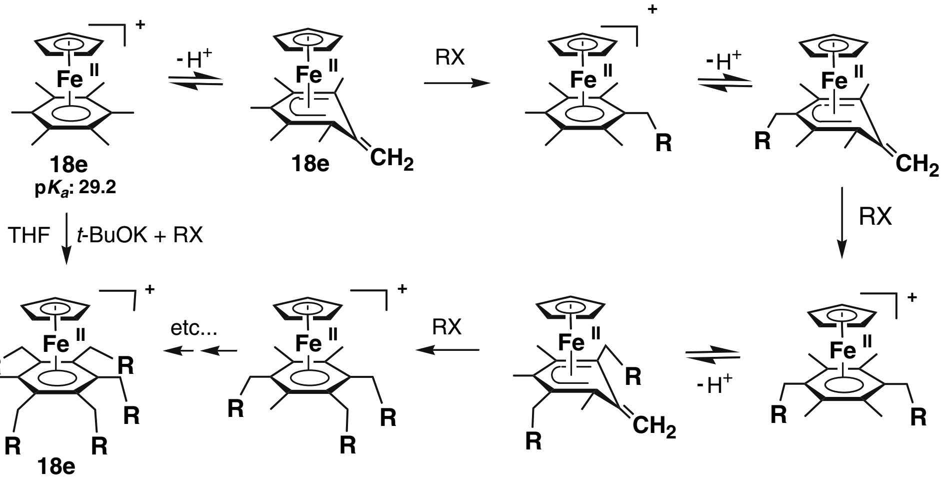
The same reaction with the mesitylene complex $[Fe^{II}Cp(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]^+[PF_6]^-$ with excess allyl bromide and KOH at room temperature quantitatively yields the nona-allyl complex resulting from the deprotonation–allylation sequence of all the nine benzylic C–H bonds due to the absence of steric inhibition around the arene ligand (Scheme 4) [10].

This chemistry has become extremely useful in dendrimer synthesis, because the complexes $[Fe^{II}Cp(\eta^6\text{-arene})]^+[PF_6]^-$ are very robust and easy to handle in air. In addition, the arene complexes are very easy to make in large scales in high yields by reaction of ferrocene with a large variety of arenes [11]. The perallylation and perbenzylation reactions of these complexes in the presence of excess KOH and organic halide are so easy as well under ambient conditions in large scales and essentially quantitative. These perfunctionalized arene iron complexes

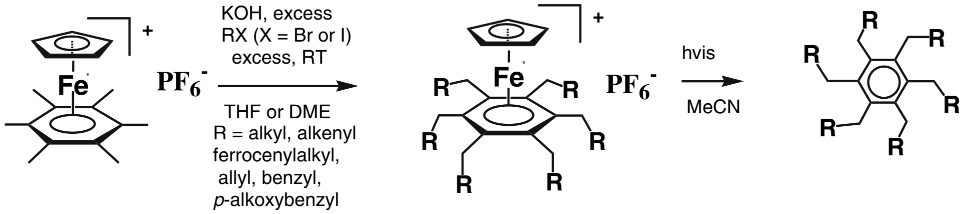
Scheme 1 Mild C–H activation by O_2 in the 19-electron complexes $[Fe^{I}Cp(\eta^6\text{-}C_6R_5CH_3)]$



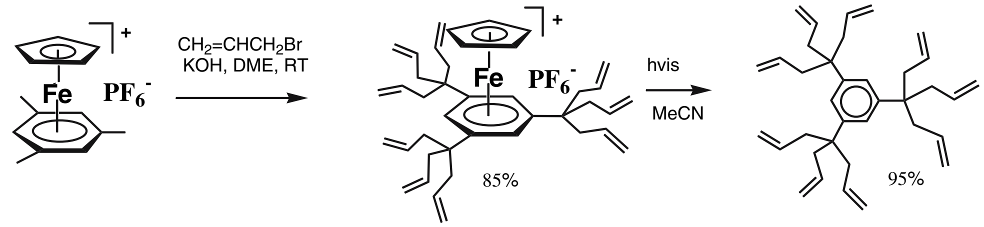
Scheme 2 Facile, iterative one-pot hexamethylation of $[Fe^{II}Cp(\eta^6\text{-}C_6Me_6)][PF_6]$, complete in one minute in the presence of CH_3I in THF



For instance, with RX = MeI: overall one minute (with spontaneous gentle reflux)



Scheme 3 General scheme for the CpFe$^+$-induced hexafunctionalization of C_6Me_6 using an excess of KOH and organic halide under ambient conditions



Scheme 4 CpFe$^+$-induced nona-allylation of mesitylene in the presence of excess KOH and allylbromide in THF under ambient conditions

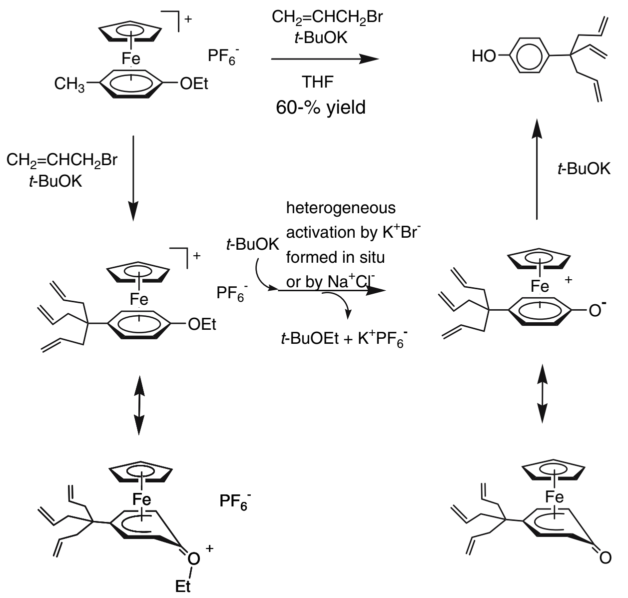
undergo quantitative decomplexation upon visible-light irradiation, readily providing organic star- and dendrimer cores [12].

3 From Simple C–H Activation to an easy and Efficient Dendrimer Construction

A challenge was to extend this activation system to functional arene complexes, and in particular the perallylation of the ethoxytoluene complex using allyl bromide and *t*-BuOK in THF under sub-ambient conditions provided the very useful "phenoltriallyl" dendron in up to 60% yield [13]. Interestingly, *t*-BuOK plays three roles, first that of a base, then that of nucleophile cleaving the exocyclic ether C–O bond, then finally acting as an electron transfer reagent generating the transient 19-electron Fe^I species that immediately collapses, due to the presence of the exocyclic oxygen atom that rapidly displaces the arene ligand to give the final iron-free arene dendron [14]. Although the intermediate triallylated arylether and phenolate complexes were both isolated, the aryl ether cleavage step cannot proceed using *t*-BuOK alone, because it is too weak of a nucleophile. It is KBr, formed in the first step and heterogeneously activating the C–O bond, that allows this step to proceed, and the action of KBr can be replaced by added NaCl as well (Scheme 5) [14b].

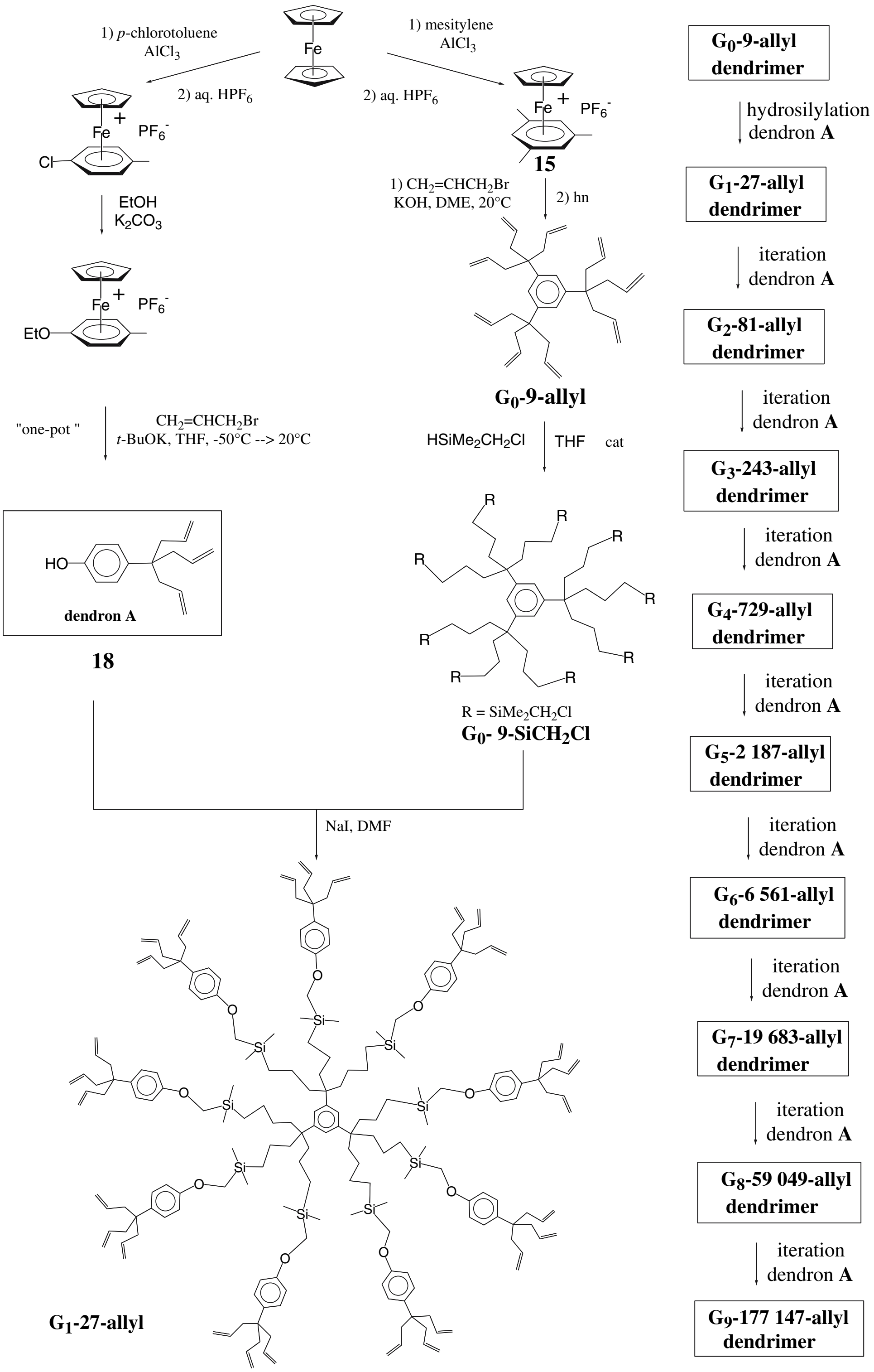
With a nona-allyl arene core and the "phenoltriallyl" brick, dendrimers containing 3^{n+2} terminal allyl tethers (n = generation number) could be constructed [15] using the 1 → 3 C connectivity pioneered by Newkome with arborols [16] by a series of hydrosilylation–Williamson reactions. The hydrosilylation was carried out using chloromethyldimethylsilane [17] and Karsted catalyst at 40 °C whereas the Williamson step was performed between the chloromethyl-terminated dendrimers and phenoltriallyl using a catalytic amount of NaI and K_2CO_3 in DMF at 80 °C. Each step was checked by ^{1}H, ^{13}C and ^{29}Si NMR and gave virtually pure dendrimers at the accuracy of NMR. MALDI TOF mass spectra show, however, that if the molecular peak largely predominates for the second generation 81-allyl dendrimer, the defects predominate in the spectrum of the 3rd generation 243-allyl dendrimer and the molecular peak is not even seen in that of the 4th generation 729-allyl dendrimer, which shows massifs near the molecular peak (Scheme 6).

The dendrimers were characterized by size exclusion chromatography until generation five showing a



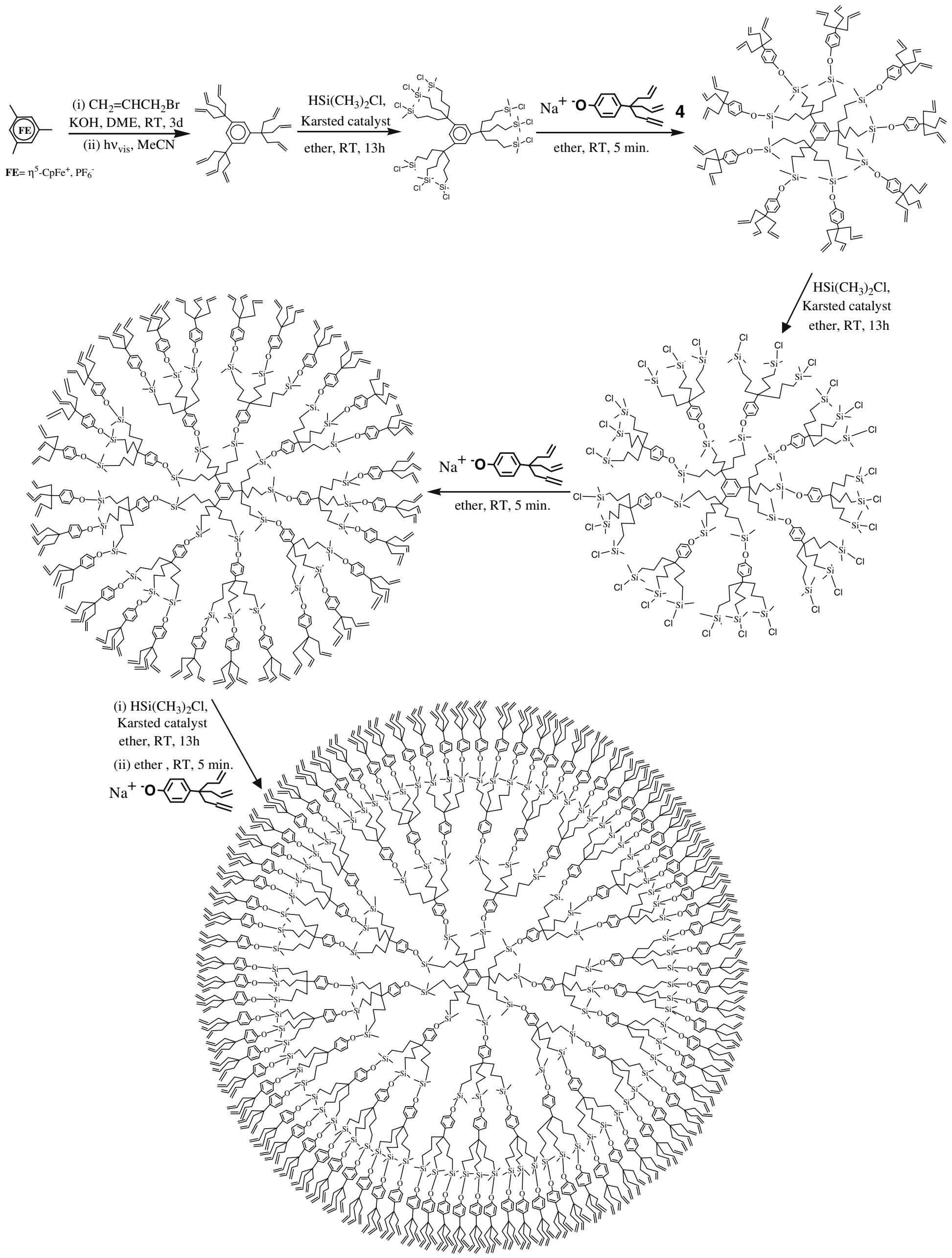
Scheme 5 One-pot synthesis of the "phenoltriallyl" dendron p.HOC$_6$H$_4$C(allyl)$_3$ starting from [FeCp(η^6-C$_6$H$_5$OC$_2$H$_5$)][PF$_6$], *t*-BuOK and allylbromide in THF, under sub-ambient conditions. Note the three roles of *t*-BuOK: base, then activated nucleophile, then electron-transfer reagent

Scheme 6 Construction of giant dendrimers starting from ferrocene with 3^{n+2} terminal tethers (n = generation number) until G_9 (theoretical number of 3^{11} terminal tethers). Each dendrimer along the construction was characterized by ^1H, ^{13}C and ^{29}Si NMR (till G_9), MALDI TOF mass spectrometry (till G_4), SEC (PI = 1.00 to 1.02 till G_5), TEM and AFM (till G_9) showing the steady size increase



polydispersity between 1.00 and 1.02, atomic force microscopy showing the progression of the height of the monolayer from the first to the 9th generation and transmission electron microscopy of the polyiodo derivative of the last generation. Although the number of defects becomes larger and larger as the generation number increases, it may be estimated that the last generation reaches a number of terminal tethers of the order of 10^5. Beyond generation 5 (theoretical number: $3^7 = 2187$ terminal tethers), it is compulsory that further dendritic construction reactions occur inside the dendrimers interior because the small termini must back-fold toward the center in order to avoid the bulk at the periphery and fill the interior cavities. Thus the dendrimer construction becomes limited by the volume rather than by the surface. The reactions become slower and slower and the yields are lower as the generation number increases beyond generation 5 [15].

Thus the next challenge is the synthesis of large dendrimers with peripheral functional groups that will be reported shortly. Another challenge is the one-pot synthesis of dendrimers using such a strategy [18]. This was shown to be possible if chlorodimethylsilane [19] was used instead of chloromethyldimethylsilane in the construction scheme. Indeed, the terminal Si–Cl bonds formed at the periphery of the dendrimer subsequent to hydrosilylation are much more reactive in the Williamson reaction with phenolates than the chloromethylsilyl termini, which permits the one-pot synthesis of up to the 243-allyl G_3 dendrimer. The Si-phenolate link is less robust than the Si–CH_2-phenolate link, but is stable enough for extensive characterization. Such fragile dendrimers might be useful for applications requiring the decomposition of the dendrimer interior after using it as a template, for instance in materials chemistry (Scheme 7) [18].



Scheme 7 One-pot synthesis of polyolefin dendrimers till G_3 ($3^5 = 243$ terminal allyl groups) using the silane $HSiMe_2Cl$

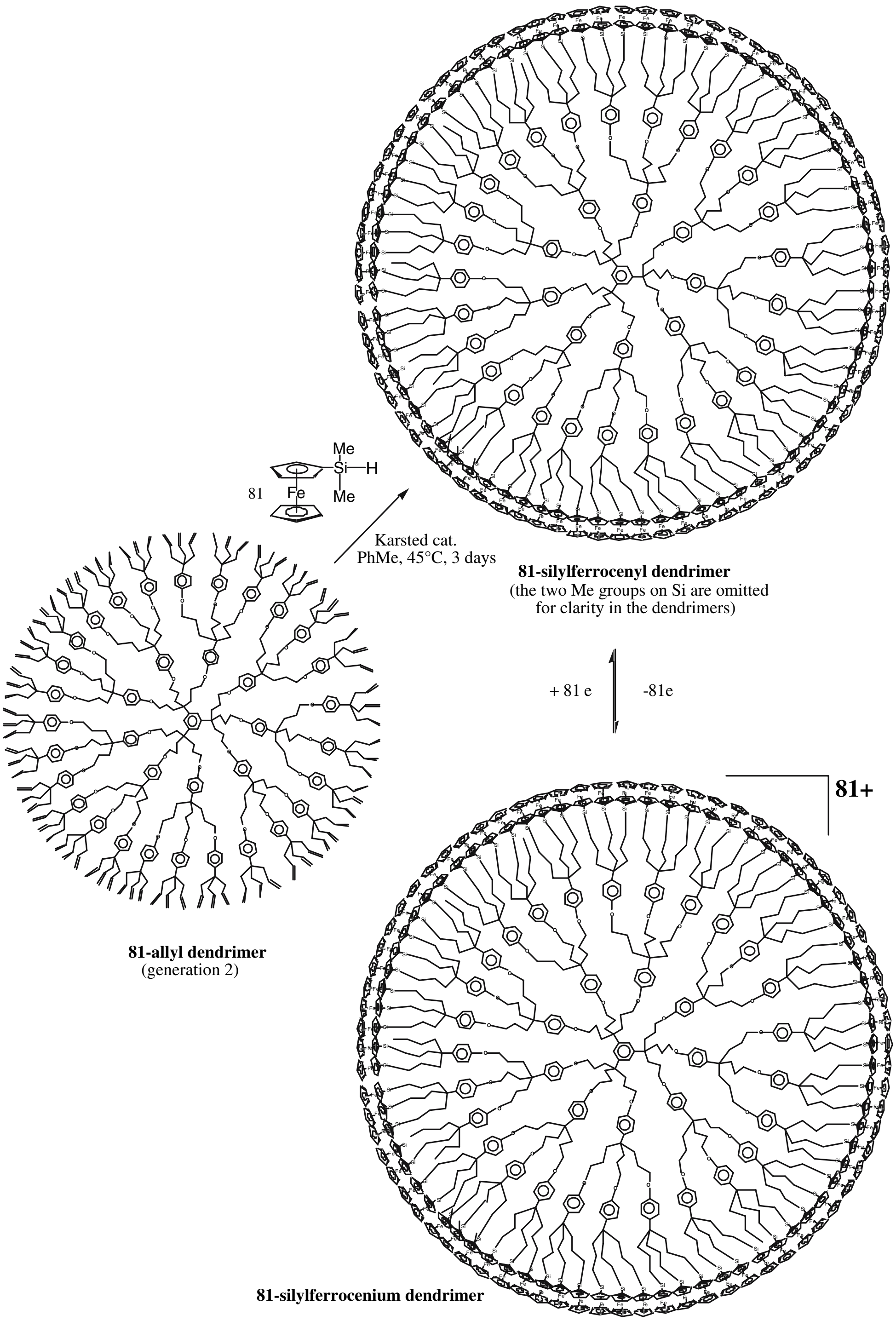
4 Ferrocenyl Dendrimers

The first ferrocenyl dendrimers designed for function were synthesized by reaction of amine-terminated dendrimers with ferrocenoyl chloride, which yielded amidoferrocenyl dendrimers that were redox exo-receptors of oxo-anions [20]. It was subsequently found that silylferrocenylation of polyolefin dendrimers yielded polysilylferrocenyl dendrimers (Scheme 8).

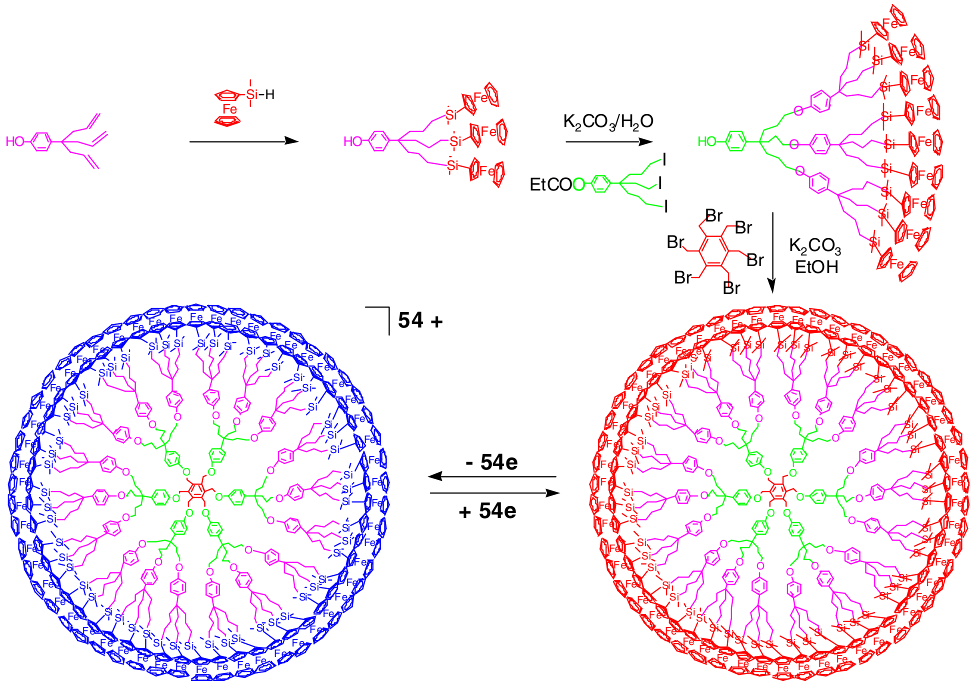
Likewise, the silylferrocenylation of the “phenoltriallyl” brick yielded triferrocenyl dendrons that could be condensed onto a polyhalogeno core to form polyferrocenyl dendrimers (Scheme 9) [21].

With gold-nanoparticle-cored dendrimers, it was found that the silyl group was an excellent alternative to the

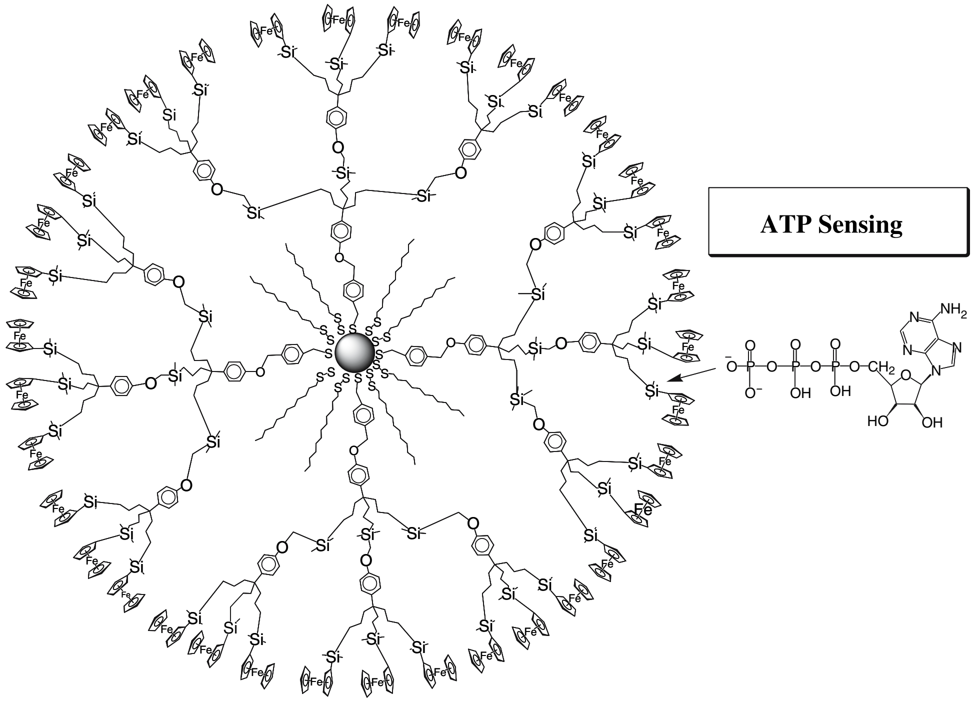
Scheme 8 Ferrocenylsilylation of the “phenoltriallyl” dendron for the construction of ferrocenyl-terminated dendrimers



Scheme 9 Ferrocenylsilylation of the 81-allyl G_2 dendrimer for the synthesis of ferrocenyl-terminated dendrimers



Scheme 10 Gold-nanoparticle-cored dendrimer terminated by ferrocenylsilyl group that recognize and sense oxo-anions such as $H_2PO_4^-$ and ATP



amido group when it was attached to the ferrocenyl termini for the recognition of oxo-anions including ATP [22]. The factors involved in the redox recognition are the electrostatic attraction between the anion and the ferrocenium cation upon anodic oxidation and the supramolecular bonding between the amido group (hydrogen bonding) of the silyl group (Si hyper valence). The amidoferrocenyl or silylferrocenyl monomers do not show any effect, however. Therefore, the dendrimer topology is important for recognition of oxo-anions. The appropriate encapsulation of the anionic host between the dendritic tethers is a key factor that very much increases the interaction between the functional ferrocenyl termini and the guest (Scheme 10).

5 Engineering the Dendrimer Family with Peripheral Ferrocenyltriazole Ligands: “Click” Dendrimers and Metallodendrimers for Oxo-anion and Transition-metal Cation Sensing

The 1,2,3-triazole is an ideal choice for the interaction with many substrates that have Brönsted or Lewis acid properties including transition metals and their complexes. Thus the encapsulation of such guests should prove feasible by introducing such triazole groups on the dendrimer tethers. The 1,2,3-triazole group is readily formed by “click” chemistry recently reported by Sharpless to catalyze with Cu^{I} the regioselective Huisgens reaction between azido derivatives and terminal alkynes [23]. We used the dendrimer family that was constructed as indicated above and substituted the terminal halogeno group by azido upon reaction with NaN_3. These azido-terminated dendrimers were engaged in reactions with ferrocenyl acetylene in order to locate the redox sensor directly on the triazole ring for adequate sensing of the interaction of guests with the triazole heterocycle by perturbation of the redox potential of the ferrocenyl system (Scheme 11).

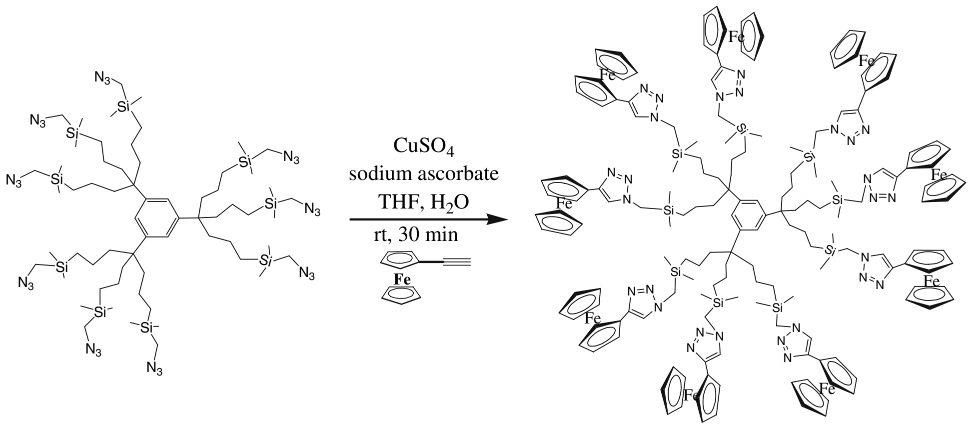
Ferrocenyl terminated dendrimers are known as very good sensors of oxo-anions with positive dendritic effects, i.e. the magnitude of the recognition effect increases together with generation number, because the dendrimer topology of higher generations involves narrower channels for a better interaction with the dendritic site on the tethers. Thus oxo-anions including ATP, a DNA fragment, are well recognized by the “click” ferrocenyltriazolyl dendrimers. The additional electron density brought by the oxo-anions makes the ferrocenyl oxidation easier, i.e. at less positive oxidations potentials. On the other hand, the interaction with acetonitrile complexes of several transition metals (Cu^{I}, Cu^{II}, Pd^{II}, Pt^{II}) withdraws electron density from the ferrocenyltriazolyl system, the ferrocenyl oxidation is rendered more difficult, and its wave is found at more positive potentials (Scheme 12) [24].

6 The Click Reaction as a Useful Iterative Method for Dendrimer Construction

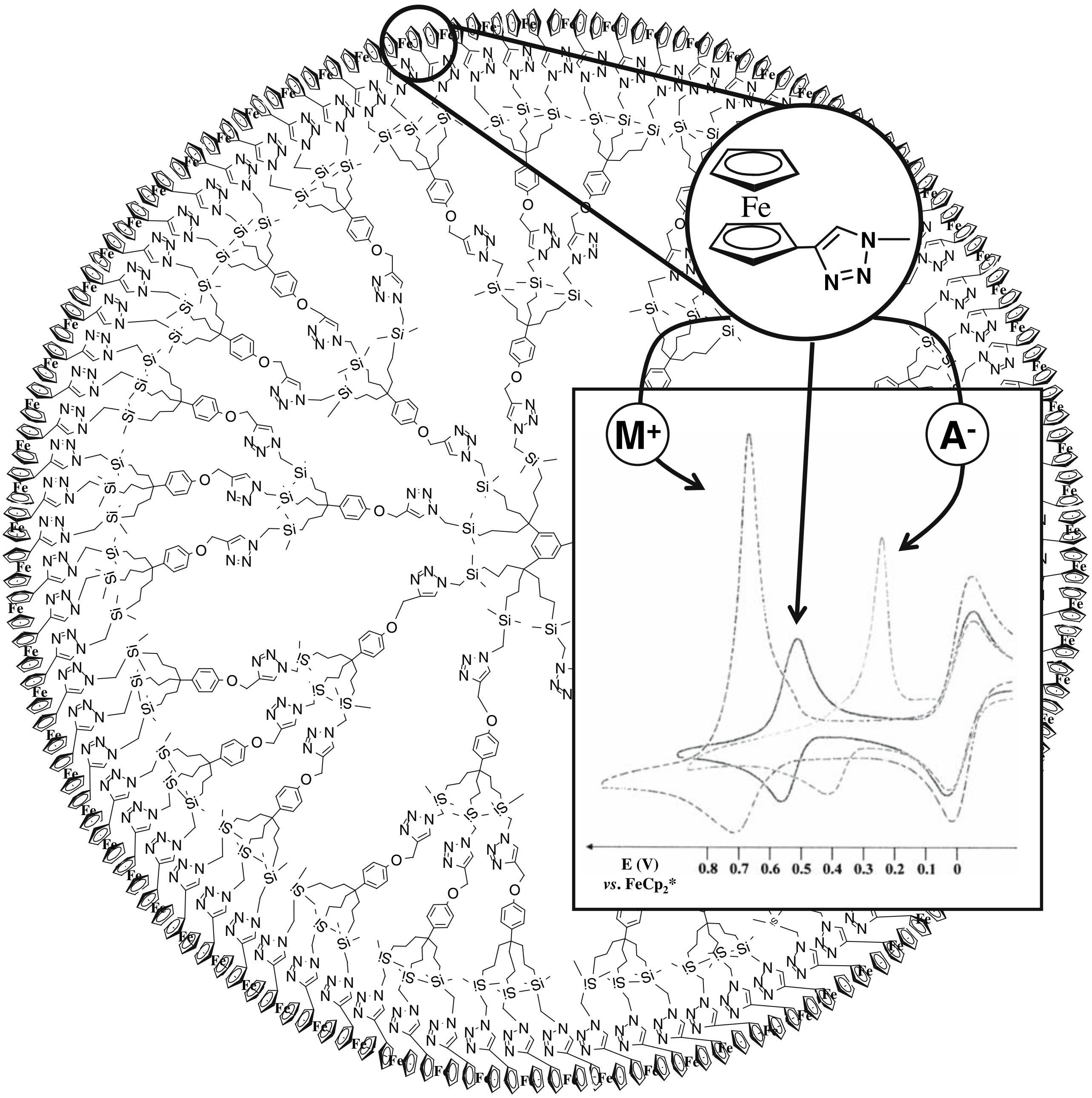
In the preceding example, the “click” reaction was used for peripheral dendrimer functionalization. We then addressed the challenge of using the “click” reaction iteratively for divergent dendrimer construction. For this purpose, the “phenoltriallyl” brick used above was propargylated at the focal point before “click” reaction with an azido-terminated dendritic core as above. After the “click” reaction, the polyolefin dendrimer formed in which the number of terminal tethers has been multiplied by three is submitted to hydrosilylation with chloromethyldimethylsilane as in our classic dendrimer construction, then the terminal chloro groups are substituted by azido groups for further iteration of the “click” reaction with the propargylated dendron (Scheme 13) [25].

7 Dendrimers Containing Triazole Ligands and Ferrocenyl Termini as Useful Templates for Transition-metal Ions and Transition-metal Nanoparticles

The triazole ligands were introduced in these dendrimers in order to bind transition-metal cations before their reduction to metal (0) to form nanoparticles that are either stabilized inside the dendrimer or, if the dendrimer is too small, that are stabilized by the dendrimer without encapsulation. The ferrocenyl groups located at the dendrimer periphery just near the triazole rings allow titrating the metal cations that interact herewith. Palladium (II) was coordinated to the triazole ligands in the dendrimer interior using $Pd(OAc)_2$, then reduced to Pd(0) using $NaBH_4$ or methanol. The coordination of $Pd(OAc)_2$ onto the triazole ligands was monitored by cyclic voltammetry, showing the appearance of a new wave corresponding to the ferrocenyl groups attached to Pd(II)-coordinated triazoles. The outcome was a one-to-one stoichiometry that allowed designing a given



Scheme 11 Synthesis of a “click” ferrocenyl dendrimer (G0)

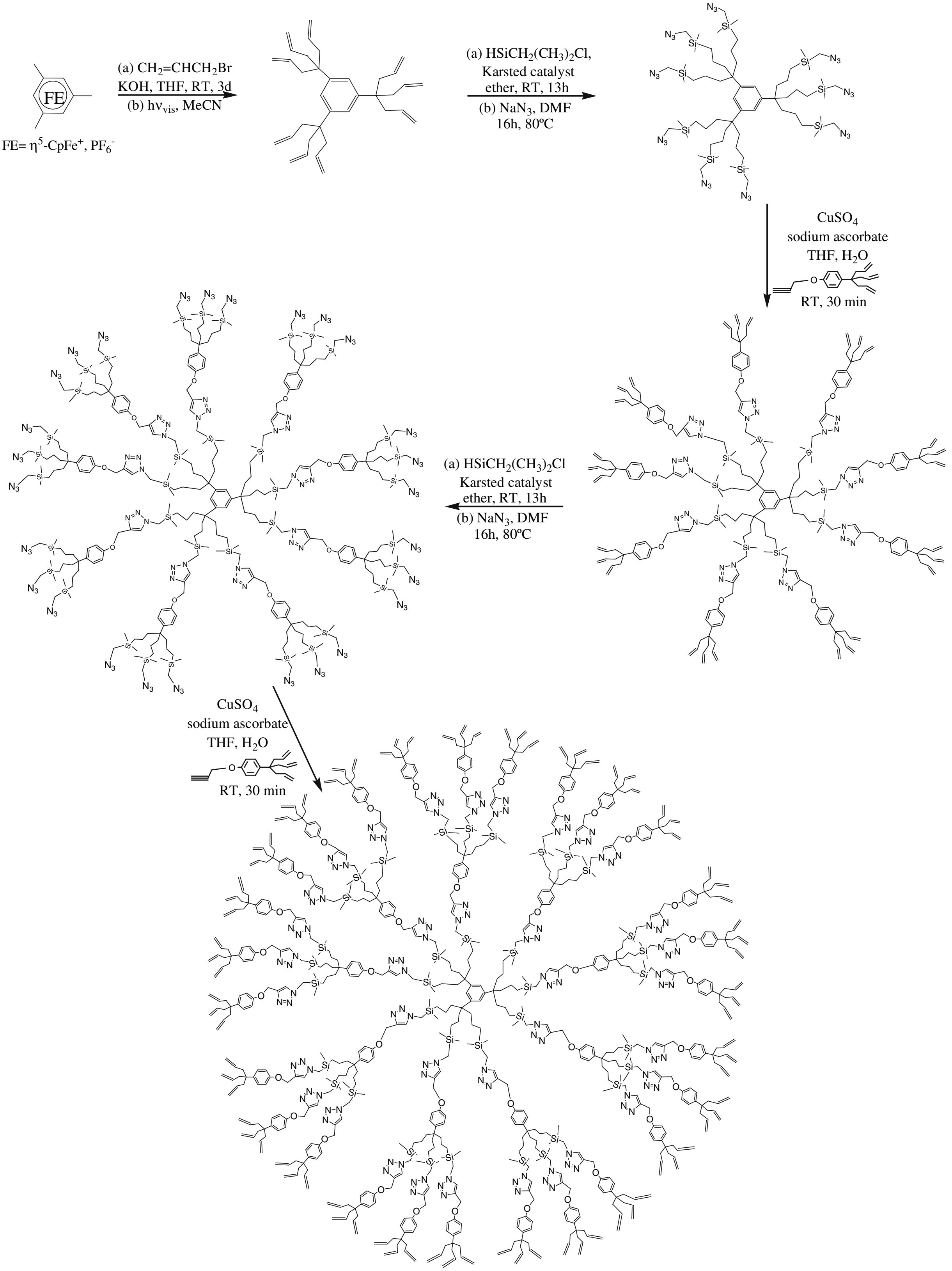


Scheme 12 Second-generation "click" ferrocenyl dendrimer (81 terminal ferrocenyltriazolyl groups) that recognizes both oxo-anions including ATP and transition-metal dications (Cu^{I}, Cu^{II}, Pd^{II}, Pt^{II}) with positive dendritic effect (i.e. recognition, characterized by the shift of potential of the ferrocenyl CV wave, works all the better as the dendrimer generation is higher)

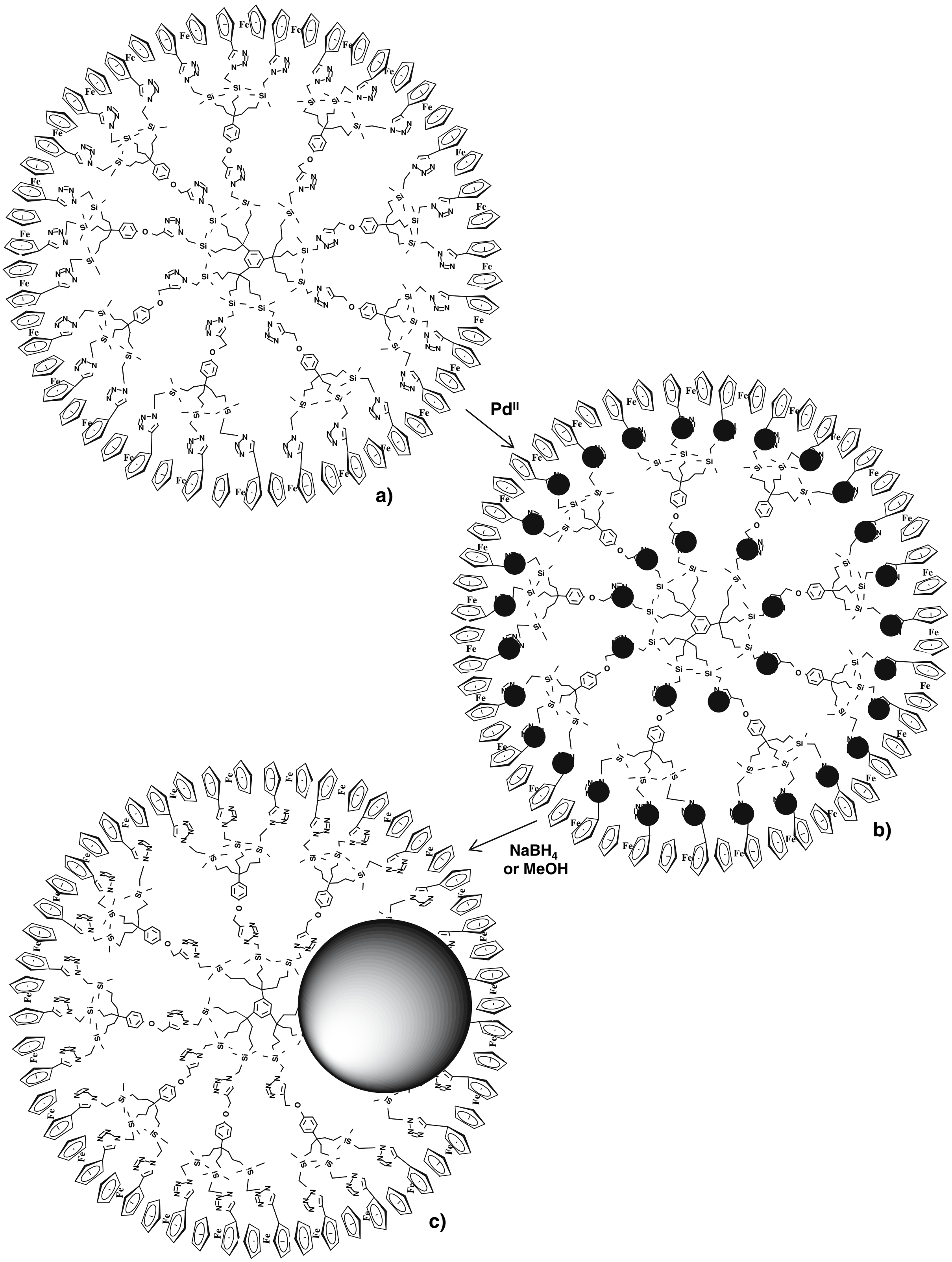
number of Pd atoms in the Pd nanoparticles if the dendrimer is large enough for nanoparticle encapsulation. This point is very important for applications (Scheme 14) [25].

8 Application in Catalysis of "Click" Dendrimers and Dendrimer-Stabilized Nanoparticles

Nanoparticles are attracting increasing attention as catalysts from both the homogeneous- and heterogeneous catalysis communities, because they are "ligandless" catalyst avoiding toxic phosphines, and show remarkable activities and selectivities [26]. Nanoparticles can be stabilized by an extremely large variety of supports from organic to inorganic [27]. Polymers have been among the most popular supports for nanoparticle catalysts [28], thus dendrimers also stabilize them, and dendrimer stabilization can proceed either by encapsulation [29] or, if the dendrimer is too small, by peripheral stabilization of the nanoparticle surrounded by a number of dendrimers [30].



Scheme 13 Iterative construction of a G_2 “click” dendrimer using a hydrosilylation-click-reaction sequence

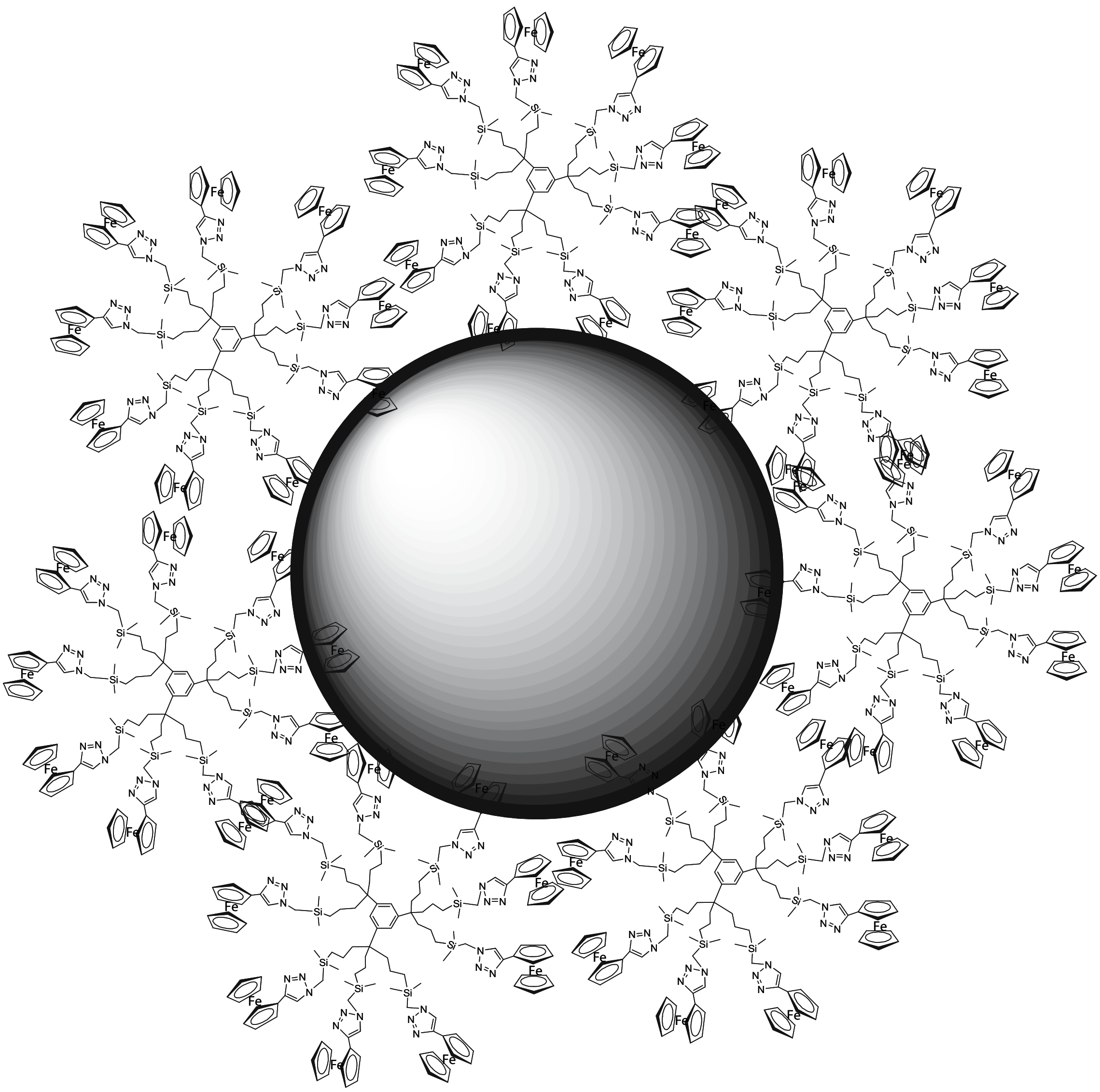


Scheme 14 Coordination of the triazole ligand by $Pd(OAc)_2$ monitored by ferrocenyl redox sensing followed by Pd(II) reduction to dendrimer-encapsulated Pd (0) nanoparticles used further in catalysis. The variety of nanoparticle sizes obtained with this strategy is crucial for catalyst optimization and mechanistic investigation

Thus commercial polyamidoamine and polypropylene imine have been extensively used to stabilize nanoparticle catalysts [31].

Click-dendrimer-stabilized nanoparticles are a new family of dendrimer-stabilized nanoparticles that is particularly suitable for catalytic studies [25, 32]. Different Pd nanoparticles were synthesized from the dendrimers of generations 0 (9 tethers) to 2 (81 tethers). Transmission electron microscopy shows that generations G_1 and G_2 form dendrimer-encapsulated nanoparticles whose sizes correspond to Pd nanoparticles that contain the same number of Pd^0 atoms as that of Pd^{II} ions initially coordinated to the triazoles inside the dendrimer, whereas G_0 is too small to encapsulate the nanoparticle formed. In this case, the nanoparticle is surrounded by a number of dendrimers that provide stabilization (Scheme 15).

The collection of different nanoparticles having different designed sizes is crucial to the study of the mechanisms in nanoparticle catalysis. These “click” dendrimer-stabilized nanoparticles are efficient catalysts for selective olefin hydrogenation under ambient conditions, and the turnover frequencies, turnover numbers and yields depend on the nanoparticle size. The smallest nanoparticles (from G_1) are the most active ones, in agreement with a classic hydrogenation mechanism entirely proceeding at the nanoparticle surface [32]. On the other hand, the turnover numbers, turnover frequencies and yields are independent on the type of nanoparticle stabilization and sizes of the nanoparticles for the Suzuki cross coupling reaction between chlobenzene or bromobenzene and $PhB(OH)_2$. Moreover, the TON increases when the amount of nanoparticle catalyst is decreased or when the solution is diluted.



Scheme 15 Pd nanoparticle surrounded and stabilized by several small G_0 dendrimers

The efficiency reaches 54% yield using 1 ppm Pd nanoparticles, i.e. the amount of nanoparticle catalyst is homeopathic. On the other hand, with high loading of catalyst, the yield is not quantitative, reaching only 70% at 1% Pd atom catalyst. These phenomena are taken into account by a leaching mechanism whereby one or two Pd atoms escape from the nanoparticle surface subsequent to the oxidative addition of the aryl halide onto the nanoparticle surface, then become extremely active in solution until it is quenched by the mother nanoparticle [32]. A similar mechanism had been proposed earlier by de Vries for the Heck reaction at high temperature (150–170 °C) [33].

9 Conclusion and Outlook

The simple organometallic activation of benzylic C–H bonds by air in extremely facile conditions (−78 °C) led us to efficient constructions of nanoarchitectures for functions. The synthesis of a variety of ferrocenyl-terminated dendrimers then provided the opportunity to reveal the compared performances of the functional groups attached the peripheral ferrocenyl groups as exo-receptors. Indeed, the reversibility of the ferrocenyl wave could be largely used in redox molecular recognition of oxo-anions including ATP. The derivatization of large ferrocenyl dendrimers easily yields stable modified electrodes that are very useful. Sensing is strongly dependent on the type of supramolecular interaction localized near by the ferrocenyl redox center. With the most recent “click” dendrimers with which the recognition can be achieved for both oxo-anions and transition-metal cations, redox recognition was very useful to determine the number of Pd^{II} ions coordinated into the dendrimer on the triazole ligands. The precise sizes of Pd nanoparticles designed in this way led to delineation of mechanistic experiments and catalyst optimization that significantly contributes to the knowledge and performance of Pd nanoparticle catalysis. Studies along these lines are ongoing.

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